

Chemical kinetics and dynamics of plasma-assisted pyrolysis of assorted non-nuclear waste

Dr B V Babu

Professor of Chemical Engineering &
Dean – Educational Hardware Division (EHD)
Birla Institute of Technology and Science (BITS)
PILANI – 333 031 (Rajasthan) India

Phone: 01596-245073 Ext 259/212

Fax: 01596-244183

E-mail: bvbabu@bits-pilani.ac.in; profbvbabu@gmail.com

Homepage: <http://discovery.bits-pilani.ac.in/discipline/chemical/BVb>

1. Introduction

Waste management is an important issue in both developed and developing countries nowadays. Today's society uses, and quickly discards, a large volume of an increasingly diverse range of polymeric materials. Organic wastes, such as used rubber and plastic are among the waste materials that represent problematic wastes on one hand and valuable potential as secondary raw materials on the other hand (Huang and Tang, 2007). Most conventional chemical methods cannot deal with Municipal Solid Waste (MSW) due to the diversity of its composition, which range from simple thermoplastics to complex thermosets and composites (Guddeti *et al.*, 2000). Nowadays MSW also contains outdated computer parts and electronic items. Printed Circuit Boards (PCB) are a major part of the waste from electrical and electronic equipment (WEEE); utilization, recycling, and final disposal of these products have become important issues (Hung-Lung *et al.*, 2007).

Apart from the municipal solid waste, biomass generated from various agriculture residues (majority coming from rice and wheat straw, corn stalk, cotton stems and bagasse) are wastes, which are used as primary sources of energy for domestic purposes by low-efficiency methods of direct combustion (Shuangning *et al.*, 2006). Biomass is often regarded as a renewable, storable and transportable energy source; it is available in various forms such as wood, agricultural and forest residues, and garbage. Biomass energy is neutral with respect to CO₂ emission, and can significantly alleviate the greenhouse effect caused by fossil fuel consumption (Tang and Huang, 2005).

To alleviate part of our energy crisis and environmental degradation, it has become imperative to make use of appropriate technologies for recovery of resources from non-conventional sources like MSW and biomass residues. Pyrolysis and gasification are efficient ways for biomass utilization. However, the gas yield from conventional pyrolysis technology is normally below 40 wt% of biomass feed and the accompanying corrosion to the equipments caused by the high content of tar vapor contained in the gas

phase is serious (Tang *et al.*, 2003). These problems are difficult to overcome due to only limited control of the product composition in pyrolysis and gasification processes. Incineration of organic waste may utilize the energy content of organic waste but is associated with the generation of SO₂, NO_x and other hazardous emissions (Huang and Tang, 2007).

Thermal plasma technology has been under active development for a long time. The technology is now well established in metallurgical processing, materials synthesis etc. The extremely high temperatures generated by plasma torches have spurred development of their application to waste processing, as they are capable of significantly decreasing the waste volume to a non-leachable residue. By far the most important application of thermal plasma waste treatment is focused on the destruction of hazardous wastes rather than recycling because of economic issues. Nevertheless, in recent years, the interest in energy and resource recovery from waste has grown significantly, and substantial research studies on the use of plasmas in organic waste treatment have been reported in the literature (Huang and Tang, 2007).

Pyrolysis has the potential of transforming solid wastes into useful recyclable products, but conventionally leads to a wide spectrum of pyrolysis products, which are difficult to be separated and utilized. Recently, attention has been paid to plasma-assisted pyrolysis and plasma gasification. Guddeti *et al.* (2000) used an inductively coupled plasma technology for the depolymerization of the polyethylene. Huang *et al.* (2003) used waste rubber as the raw material for production of syngas (CO₂ and H₂) by thermal plasma pyrolysis, and the combustible heat value of the produced gas was 5-9 MJ/m³. Tang and Huang (2005) developed a laboratory-scale capacitively coupled radio frequency (RF) plasma pyrolysis reactor for wood and char gasification. Shuangning *et al.* (2006) developed a plasma heated laminar entrained flow reactor in order to study the volatilization characteristics of biomass particles at flash heating rates. Corn stalk and wheat straw is used as a raw material. And very recently plasma pyrolysis method is employed to recycle the metals and brominated compounds blended into printed circuit boards (Hung-Lung *et al.*, 2007).

Plasma pyrolysis has a number of unique advantages over conventional pyrolysis. It provides high temperature and high energy for reaction. The reaction sample is heated up to a high temperature rapidly, and some reactions occur that do not appear in conventional pyrolysis. It is an appropriate method for polymer pyrolysis. It also produces a gas with low tar content and high heating value, which can be applied well to gas turbines for power generation or used as a synthesis gas for hydrogen production (Tang and Huang, 2005). There is a tremendous scope for applying plasma assisted pyrolysis of assorted non-nuclear waste such as biomass, printed circuit boards, organic waste, medical waste etc., for obtaining useful energy.

2. Plasma Properties

Plasma is considered by many to be the fourth state of matter, following the more familiar states of solid, liquid and gas. A gas converts into the plasma upon addition of

high energy. In other words, plasma is an ionized gas resulting from an electrical discharge (Huang and Tang, 2007). Gases will not conduct electricity under normal conditions, but when a very high voltage is applied the insulating properties begin to break down. As electricity starts to flow through the gas it heats up and it begins to conduct more and hot plasma is formed. Well-known examples of plasmas are the sun and the lightning. However, these are examples of natural and uncontrolled plasmas. Man made controlled plasmas have been used in industry for many years and for a number of diverse applications, such as chemical analysis and the cutting of metals (David and Peter, 2007).

Plasma, the state of matter formed by removing the bound electrons from atoms, is an electrically conducting fluid consisting of charged and neutral particles. The charged particles have high kinetic energies. When the ionized species in the plasma, recombine with the stripped electrons, significant amounts of energy in the form of ultraviolet radiation are released. The particle kinetic energy takes the form of heat and can be used for decomposing chemicals. In addition, the presence of charged and excited particles renders the plasma environment highly reactive, which can catalyze homogeneous and heterogeneous chemical reactions (Nema and Prasad, 2002).

There are mainly two types of laboratory plasma exist: (1) high temperature or fusion plasmas, and (2) low temperature or gas discharges. High temperature plasma implies that all species (electrons, ions and neutral species) are in a thermal equilibrium state. Low temperature plasma is divided into thermal plasma, also called quasi-equilibrium plasma, which is in a local thermal equilibrium (LTE) state, and non-thermal plasma, also called non-equilibrium plasma or cold plasma. The state parameters of each type of plasma are listed in Table – 1 (Huang and Tang, 2007).

Table-1. Classification of Plasmas

Plasma	State	Example
High temperature plasma (Equilibrium Plasma)	$T_e = T_i = T_h, T_p = 10^6 \text{ K} - 10^8 \text{ K}$ $n_e \geq 10^{20} \text{ m}^{-3}$	Laser fusion plasma
Low Temperature Plasma		
Thermal Plasma (Quasi-equilibrium plasma)	$T_e \approx T_i \approx T_h, T_p = 2 \times 10^3 \text{ K} - 3 \times 10^4 \text{ K}$ $n_e \geq 10^{20} \text{ m}^{-3}$	Arc Plasma, atmospheric RF discharge
Non-thermal plasma (Non-equilibrium plasma)	$T_e \geq T_h \approx 3 \times 10^2 \text{ K} - 4 \times 10^2 \text{ K}$ $n_e \approx 10^{10} \text{ m}^{-3}$	Corona discharge

T_e = electron temperature; T_i = ion temperature; T_h = Neutral temperature; T_p = Plasma temperature; n_e = Electron density

3. Plasma Generators

Thermal plasma generation can be achieved using a direct current (DC) or an alternating current (AC) electrical discharge or using a radio frequency (RF) induction or a microwave (MW) discharge. A DC arc discharge provides a high energy density and high temperature region between two electrodes. RF plasma torches utilize inductive or capacitive coupling to transfer electromagnetic energy from the RF power source to the plasma working gas.

3.1 DC Arc Plasma Generator

The DC arc plasma generator consists of a water-cooled tungsten tip with an auxiliary copper anode surrounding it. The water-cooled anode cup is placed in front of the cathode. Both anode and cathode are surrounded by a magnetic field coil, which produces an axial magnetic field parallel to both the anode and cathode axes. The whole torch assembly is mounted on a flange of around 100 mm diameter in a side port. The arc is initiated between the cathode and the auxiliary anode, and then transferred to the copper anode (Nema and Prasad, 2002).

DC arc plasma melting and waste treatment systems are generally implemented as batch processes due to their relatively short electrode lifetimes. The average lifetime of the electrodes ranges between 200 and 500 h of operation under oxidative conditions. Product contamination can also occur due to electrode erosion. This has prevented conventional DC torches with refractory metal (tungsten) cathodes from being widely used for the transferred-arc melting of reactive metals such as Ti (Guddeti *et al.*, 2000). Temperature in the core of the plasma plume can be greater than 30000 K, whereas in the marginal zones, the temperature decreases rapidly and the average operating temperature can be as high as 5000 K (Huang and Tang, 2007). Arc torches and electrodes are usually water cooled to maintain temperature. DC torch systems may be prone to 'stray-arcing' which has reportedly led to sufficient leakage of torch cooling water into the furnace to warrant replacement of the dc torch by a simpler hollow graphite electrode (Guddeti *et al.*, 2000).

In the presence of a sufficiently high gas flow; the plasma extends beyond one of the electrodes in the form of a plasma jet. The design of transferred and nontransferred arc DC torches does not favor the injection of feedstock materials directly into or through the plasma region. Excessive loading of constricted plasma jets can lead to physical and electrical instabilities in the arc and even arc extinction. Several novel center-feed hollow- or multicathode DC torches have been developed for plasma spray coating applications. These designs have not yet been scaled up to the power levels required for processing waste and the ability to feed large amounts of material through the cathode(s) without affecting the stability of the arc is questionable (Guddeti *et al.*, 2000).

A special new-type plasma torch with a DC electric arc stabilized by a combination of argon flow and water vortex is developed by Van Oost *et al.* (2006). The DC argon-water stabilized torch with W-Th cathode generates an O-H-Ar plasma with extremely high enthalpy and temperature. The anode of the torch is a rotating water-cooled copper disc, which is positioned outside the arc chamber downstream of the torch exit nozzle. Additional argon was supplied into the anode chamber to protect the anode against the flow of reaction gases. The hybrid gas-water stabilization provides the possibility of controlling the parameters of the plasma jet and the plasma composition in a wide range from high enthalpy, low-density plasmas typical for water-stabilized torches to lower enthalpy, higher-density plasmas generated in gas-stabilized torches. Both the high temperature and the composition of plasma generated in argon/water torches are highly

advantageous for the waste treatment process. The other characteristic feature of this hybrid torch is the very low mass-flow rate of plasma. As low amount of plasma carries high energy, the power needed for heating of plasma to reaction temperature is very low, and the efficiency of utilizing plasma power for waste destruction is extremely high. The torches with water stabilization have been utilized at industrial scale for plasma spraying. Due to the physical characteristics of generated plasma the spraying rates and powder throughputs achieved with these torches are several times higher than for classical gas-stabilized torches (Van Oost *et al.*, 2006)

3.2 RF Plasma Generator

RF plasma generators are very compact and deliver extraordinarily high input energy per unit volume. Unlike DC arc plasma torches, there are no locally high temperature arcs, no moving parts and no parts subject to wear. RF current and microwaves can be transferred through insulators, so the use of external electrodes is possible. In this way, the electrodes are not exposed to the severe conditions of thermal plasmas and, therefore, have a very long lifetime. RF plasma generators are commonly available at power levels of 100 kW. RF plasma generates a very diffuse plume, and the design of external electrodes favors the injection of feedstock material directly into or through the plasma region. In RF plasma jet, the temperature at the central channel reaches up to 6000 K. Table – 2 shows the typical comparison of the DC arc and RF plasma generator (Huang and Tang, 2007).

Table-2. Comparison of DC arc and RF plasma generator (Huang and Tang, 2007)

Item	DC Arc Plasma	RF Plasma
Temperature	5000 – 10000 K	3000 – 8000 K
Electrode erosion	Yes (1000- 3000 h lifetime in inert gas and 200 -500 h in oxidative conditions)	No
Cooling of plasma generator and reactor	Required	Required
Plasma ignition	Easy	Difficult
Plasma volume	Small	Medium
Gas velocity	High	High
Solid feeding position	Downstream of plasma	Upstream of Plasma
Influence of solid feeding on plasma stability	No	Yes
Efficiency of power supply devices	60-90 %	40-70 %

A laboratory-scale capacitively coupled radio frequency (RF) plasma pyrolysis reactor working in reduced pressure has been developed by Tang and Huang (2005). RF capacitively coupled plasma process is operated at low pressure (approximately 3000–8000 Pa abs) and a moderate gas temperature suitable for biomass pyrolysis. The high efficiency of plasma pyrolysis and the high efficiency of energy utilization are combined in their experimental design (Tang and Huang, 2005). Experiments have been performed to examine the characteristics of this RF plasma reactor and the products of biomass gasification. Typical experimental setup of the capacitively coupled radio frequency (RF) plasma pyrolysis apparatus is shown in Fig. 1. It consists of a radio frequency plasma source with power output 0–2000 W and a matching network. The pyrolysis reactor is a

cylindrical quartz tube surrounded by two copper electrodes, which couple power from the RF power source to the gas as it flows through the tube. The space between two electrodes can be varied to optimize the structure of the electrodes. An inert gas N₂ is entered in the reactor to purge oxygen and also serve as a working gas to generate the plasma. For continuous in-flight gasification of biomass feedstock, a screw feeder is provided on the top of the quartz tube. A cyclone separator and a filter are provided to remove the char particles from the product vapor.

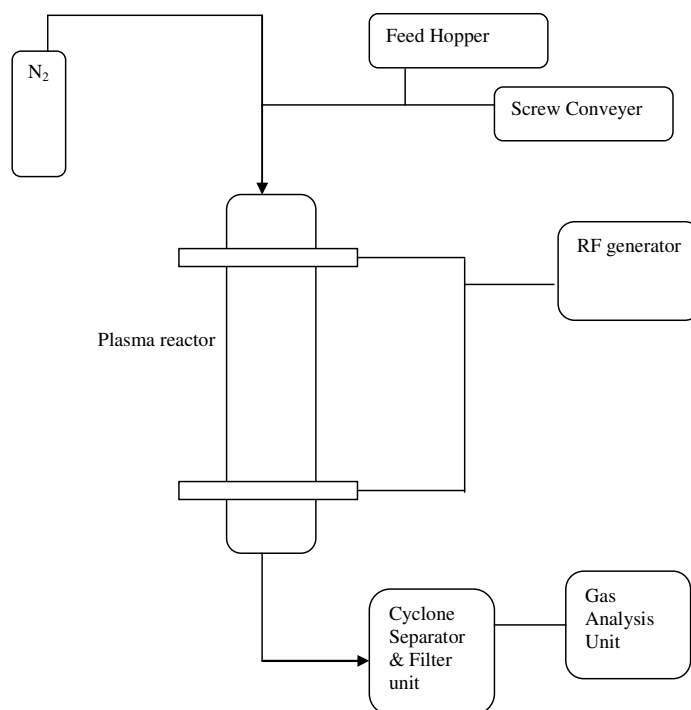


Fig. 1. Typical experimental setup of the capacitively coupled RF plasma pyrolysis unit

Polyethylene is decomposed into their monomer by inductively coupled plasma (ICP) technology by Guddeti *et al.* (2000). The gaseous products obtained are mainly mixtures of ethylene and propylene. The amount of propylene obtained was significantly higher than anticipated and was believed to be due to β -scission reactions occurring at the higher plasma temperatures. ICP torches are electrodeless, allowing use of a wider range of plasma-forming gases, including air, O₂, H₂, and even hydrocarbons, such as methane, along with Ar, Ar/H₂, Ar/He, Ar/N₂, etc.

ICP torches utilize electromagnetic induction to couple electrical energy from a power supply into a toroidal discharge. The toroidal discharge in ICP systems acts as a short-circuited, single-turn secondary winding of a transformer, the primary winding being a coil within the torch body. The RF energy is dissipated through ohmic heating of the plasma-forming gas, which reaches sufficiently high temperatures (~10,000 K or -1 eV) to achieve a high degree of ionization. The discharge can be initiated in several ways: (i) by reducing the pressure to ~10-30 kPa, such that spontaneous breakdown occurs; (ii) by

inserting an electrically conducting load, such as a graphite rod, into the torch to provide a localized source of ionization through induction heating; or (iii) applying a high-voltage Tesla coil to the central probe of the torch to generate a spark, which then ignites the plasma (Stratton *et al.*, 1999).

ICP torches can be more readily scaled up to the high power levels (>1 MW) required for high-throughput commercial systems and their continuous operation is unaffected by the electrode erosion and current carrying/cooling limitations of DC torches. ICP torch and power supply efficiencies are, however, generally lower than those of DC plasma systems. These are due primarily to the inherently lower energy-transfer efficiency of induction heating and the lower efficiency of the high-frequency power supplies used. High-frequency (MHz range) ICP systems often utilize vacuum tube-driven Class C-tuned oscillators, which have inherent efficiencies of <50%, although more efficient solid state power supplies operating at frequencies up to ~450 kHz are now being used in some of the newer high-power ICP designs (Guddeti *et al.*, 2000).

4. Pyrolysis

The thermochemical conversion of biomass (pyrolysis, gasification, combustion) is one of the most promising non-nuclear forms of future energy. It is a renewable source of energy and has many advantages from an ecological point of view (Babu and Chaurasia, 2003b). Pyrolysis is the thermochemical process that converts biomass into liquid (bio-oil or bio crude), charcoal and noncondensable gases, acetic acid, acetone and methanol by heating the biomass in the absence of air (Demirbas, 2001). The basic phenomena that take place during pyrolysis are: (1) heat transfer from a heat source, leading to an increase in temperature inside the fuel; (2) initiation of pyrolysis reactions due to this increased temperature, leading to the release of volatiles and the formation of char; (3) outflow of volatiles, resulting in heat transfer between the hot volatiles and cooler unpyrolysed fuel; (4) condensation of some of the volatiles in the cooler parts of the fuel to produce tar; and (5) autocatalytic secondary pyrolysis reactions due to these interactions (Babu and Chaurasia, 2003a).

Pyrolysis can be used as an independent process for the production of useful energy (fuels) and/or chemicals. Most biomass materials are chemically and physically heterogeneous, and their components have different reactivities and yield different products. The overall process of pyrolysis can be classified into primary and secondary stages. When a solid particle of biomass is heated in an inert atmosphere the following phenomena occur. Heat is first transferred to the particle surface by radiation and/or convection and then to the inside of the particle. The temperature inside the particle increases, causing (1) removal of moisture that is present in the biomass particle, (2) the pre-pyrolysis and main pyrolysis reaction takes place. The heat changes due to the chemical reactions, and phase changes contribute to a temperature gradient as a function of time, which is nonlinear. Volatiles and gaseous products flow through the pores of the particle and participate in the heat transfer process. The pyrolysis reactions proceed with a rate depending upon the local temperature. During the pyrolysis process, the pores of the solid are enlarged, and the solid particle merely becomes more porous because the

biomass converts into gases as discussed by Curtis and Miller (1999). According to Anthony and Howard (1976), the enlarged pores of the pyrolyzing solid offer many reaction sites to the volatile and gaseous products of pyrolysis and favor their interaction with the hot solid. Inside the pyrolyzing particle, heat is transmitted by the following mechanisms: (a) conduction inside the solid particle, (b) convection inside the particle pores and (c) convection and radiation from the surface of the pellet (Babu and Chaurasia, 2003b).

Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis (carbonization), fast pyrolysis, and flash pyrolysis. The ranges of the main operating parameters for pyrolysis processes are given in Table – 3. Conventional pyrolysis is defined as the pyrolysis that occurs under a slow heating rate. This condition permits the production of solid, liquid, and gaseous pyrolysis products in significant portions. If the aim is the production of mainly liquid and/or gaseous products, a fast pyrolysis is recommended. The achievement of fast heating rates requires high operating temperatures, very short contact times, and very fine particles. Flash pyrolysis gives mostly gaseous products due to high heating rate and very small particle size (Demirbas and Arin, 2002).

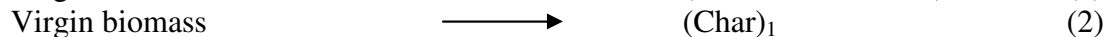
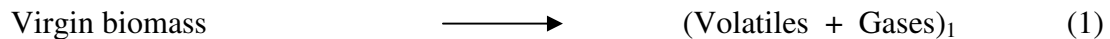
Table-3. Range of main operating parameters for pyrolysis processes

Parameters	Conventional Pyrolysis	Fast Pyrolysis	Flash Pyrolysis
Pyrolysis Temperature (K)	550-950	850-1250	1050-1300
Heating rate (K/s)	0.1-1.0	10-200	>1000
Particle size (mm)	5-50	<1	<0.2
Solid residence time (s)	450-550	0.5 -10	<0.5

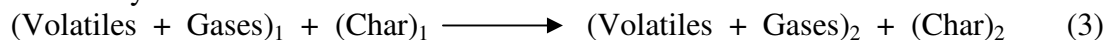
4.1 Kinetic Schemes of Pyrolysis

Different classes of mechanisms were proposed for the pyrolysis of wood and other cellulosic materials (Di Blasi, 1993). The models are classified into three categories: one-step global models; one-stage multi-reaction models; and two-stage semi-global models. The first category of models considers pyrolysis as a single-step first order reaction.

Parallel reactions:



Secondary Interactions:



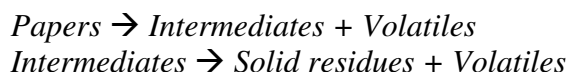
The second category of models discuss those mechanisms, which consider simultaneous and competing first order reactions in which virgin wood decomposes into different constitutes of pyrolysis products, namely, tar, char, and gases (Reactions (1) & (2)).

The third class of models considers pyrolysis to be a two-stage reaction, in which the products of the first stage break up further in the presence of each other to produce secondary pyrolysis products. Such models are presented for wood by Koufopanos *et al.*

(1991) [Reactions (1), (2) & (3)]. The scheme of reactions of Koufopoulos' models is adapted by Jalan and Srivastava (1999), Srivastava *et al.* (1994; 1996) and Babu and Chaurasia (2003a). Chan (1985) proposed a mechanism where volatiles and tar formed by primary pyrolysis undergo secondary pyrolysis. The other primary reactions of formation of char and gas from wood are parallel and competing with the tar formation reaction. Babu and Chaurasia (2003a-c; 2004a-c) did extensive modeling and simulation on pyrolysis. Kinetic Scheme proposed by Koufopoulos *et al.* (1991) for the pyrolysis of biomass based on the two-stage model is accepted and validated. The model proposed by Babu and Chaurasia (2004b) includes kinetic and heat transfer effects for the shrinking biomass particle. This model was again improved to incorporate simultaneous effects of kinetics and transport of heat, mass and momentum (Babu and Chaurasia, 2004c).

Di Blasi (1999) proposed a mathematical model, which includes transport phenomena and chemical reactions for the pyrolysis of thermoplastic polymers (polyethylene). It was found that depolymerization and melting are followed by devolatilization. Surface regression, property variation, heat convection and conduction were considered in the proposed model. Simulations were carried out for external heating conditions corresponding to fixed-bed reactors, hot-plate contact and fire-level radiation exposures.

Chao-Hsiung *et al.* (1997) performed the thermogravimetric studies of paper mixtures in municipal solid waste. The pyrolysis kinetics of a mixture of the four principal papers (uncoated and coated printing/writing papers, newsprint, and tissue paper) in municipal solid waste (MSW) was investigated. The experiments were carried out in a nitrogen environment over the temperature range of 450 to 900 K at various constant heating rates of 1, 2, and 5 Kmin⁻¹. The pyrolysis of a paper mixture is described by a two reaction model as described below:



The experimental results were satisfactorily fitted by the proposed chemical reaction kinetic equations.

4.2 Modeling of biomass pyrolysis

Several researchers have developed the mathematical models for biomass pyrolysis. Fan *et al.* (1977) developed a model for pyrolysis process, which includes heat and mass transfer effects in the particle. The reaction, however, is considered to be first order with respect to the initial particle concentration. The concentration of products cannot be analyzed from the above model, as the secondary reactions are not considered. Miyanami *et al.* (1977) incorporated the effect of heat of reaction in the above model. In the model of Bamford *et al.* (1946), the equation for heat conduction in a pyrolyzing solid is combined with those for heat generation, assuming first order kinetics. However, the effect of density as a function of time has not been considered in the above model. This model is modified by Kung (1972) in order to incorporate the effects of internal convection and variable transport properties. However, no specific kinetic mechanism is suggested to predict the concentration of various components produced during the pyrolysis process. Kansa *et al.* (1977) included the momentum equation for the motion of pyrolysis gases within the solid. But, a suitable kinetic mechanism has not been utilized

by them (secondary reactions are not considered), and the solution to the heat and momentum balance equation is based on arbitrary boundary conditions. Pyle and Zaror (1984) used the model of Bamford *et al.* (1946) and dimensionless groups to define the relative importance of the internal & external heat transfer and of the intrinsic pyrolysis kinetics. They utilized the first order kinetic model based on the density of initial biomass. In the model of Koufopoulos *et al.* (1991), the effect of density as a function of time is not considered while solving the heat transfer equation. Jalan and Srivastava (1999) have solved the heat transfer equation by neglecting the effect of specific heat and thermal conductivity of char, which are the functions of temperature as reported by Koufopoulos *et al.* (1991). The convective heat transfer coefficient is a function of the Reynolds and Prandtl numbers and is given by $h = 0.322(k/l)Pr^{1/3} Re^{0.5} W/m^2 K$, as reported by Koufopoulos *et al.* (1991). Jalan and Srivastava (1999), however, have considered that the value of h is constant at $0.322 W/m^2 K$, neglecting the effect of other parameters. Di Blasi (1993, 1996, and 1997) pointed out that a detailed transport model incorporating the kinetics, heat, and mass transfer effects are necessary to predict the effects of the widely variable physical properties (density, thermal conductivity, specific heat capacity) in the pyrolysis of biomass. However, she used a different kinetic scheme wherein the active cellulose is considered to be formed as an intermediate product. But as pointed out by Koufopoulos *et al.* (1991), it is very difficult to define physically the components or composition of the intermediates, and consequently it is not possible to measure their concentration experimentally in order to test the model rigorously.

In the present study, therefore, the model developed and modified by Babu and Chaurasia (2003a, 2003c) using physically measurable parameters and practically explainable kinetic scheme (Babu and Chaurasia, 2003b), incorporating the convective and diffusion effects is presented.

4.3 Model Description of biomass pyrolysis

Babu and Chaurasia (2004c) proposed three models for the pyrolysis of biomass under two categories namely, (1) Generalized reference model (Model-I), and (2) Simplified models (Model-II & Model-III). The three models are presented here briefly for clarity and continuity.

4.3.1. Generalized reference model (Model-I)

The generalized model incorporated all the possible effects of kinetics, heat transfer, mass transfer, and momentum transfer. The assumptions made in developing this model are as follows:

- (1) The thermal and transport properties (porosity, thermal conductivity, specific heat, mass diffusivity) vary with the conversion level.
- (2) Heat transfer occurs by all the three modes (i.e., conduction, convection and radiation).
- (3) Gas-phase processes occur under unsteady-state conditions.
- (4) Transport of mass takes place by convection and diffusion of volatile species.
- (5) Pressure and velocity vary along the porous sample.
- (6) Local thermal equilibrium exists between solid matrix and the flowing gases.

(7) The system is one-dimensional.

(8) No moisture content and no particle shrinkage.

Utilizing the kinetic scheme as described by Koufopoulos *et al.* (1991) and with the assumptions as stated above, the generalized model (Model-I) is obtained and reported in Table – 4. The equations shown in Table – 4 are written in dimensionless forms with the help of dimensionless groups given in Babu and Chaurasia (2004c). This generalized model, consisting of equations (12)-(28), which is the most comprehensive one, is named as Model-I (generalized reference model).

4.3.2. Simplified models

These simplified models include additional assumptions other than those in the generalized reference model (Model-I). Many a times, in practical situations, the generalized models may not give good predictions. In such cases, there is a need to relax some of the assumptions made in the generalized models. Starting from the generalized model, the following two simplified models are proposed by Babu and Chaurasia (2004c) for specific cases.

4.3.2.1. First Simplified Model (Model-II)

The first simplified model (Model-II) is proposed by making an additional assumption that there is no bulk motion contribution (i.e. convective transport is neglected) to the temperature profile and the product yield predictions. In this treatment a conservation equation for the mass concentration of (gases and volatiles)₁ [equation (13)] is modified by neglecting the second term on left hand side. Hence, the first simplified model (Model-II) consists of equations (12)-(23) and (26).

4.3.2.2. Second Simplified Model (Model-III)

The second simplified model (Model-III) is proposed on the following two assumptions concerning the practical applications: (1) The basic mode of transfer inside the solid particle in the process of pyrolysis is by conduction heat transfer only. (2) The effect of porosity of the solid particle is negligible. Based on these assumptions, the conservation equation for the mass concentration of (gases and volatiles)₁ [equation (13)] and heat transfer model [equation (17)] become:

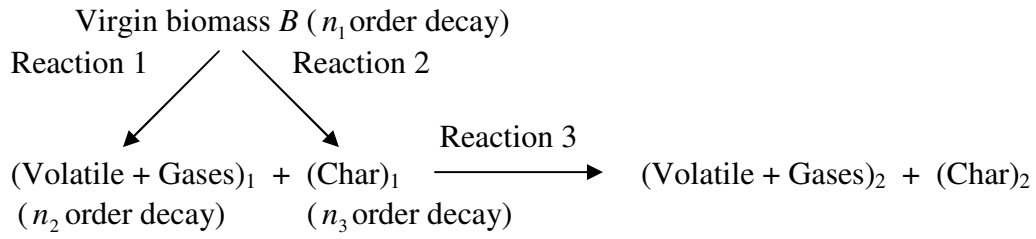
$$\frac{\partial \bar{C}_{G1}}{\partial t} = k_1 \bar{C}_B^{n_1} - k_3 \bar{C}_{G1}^{n_2} \bar{C}_{C1}^{n_3} \quad (30)$$

$$\frac{\partial \theta}{\partial \tau} = \frac{b-1}{x} \frac{\partial \theta}{\partial x} + \frac{\partial^2 \theta}{\partial x^2} + \frac{Q'' R^2 k_1}{\alpha} \quad (31)$$

Thus, the second simplified model (Model-III) consists of equations (12), (30), (14)-(16), (31), (18), (20), (22), and (23). Interestingly, this is similar to the model proposed by the Babu and Chaurasia in their earlier study (2003a), which means that the generalized reference model reduced to the model proposed by Babu and Chaurasia (2003a) under specific conditions.

Table-4. Mathematical model

Koufopoulos et al. (1991) mechanism



Particle model

Mass conservation for biomass, (gases and volatiles)₁ (char)₁, (gases and volatiles)₂ and (char)₂:

$$\frac{\partial C_B}{\partial t} = -k_1 C_B^{n_1} - k_2 C_B^{n_1} \quad (1)$$

$$\frac{\partial (C_{G1} \varepsilon'')}{\partial t} + \frac{\partial (C_{G1} u)}{\partial r} = D_{eG1} \left(\frac{b-1}{r} \frac{\partial C_{G1}}{\partial r} + \frac{\partial^2 C_{G1}}{\partial r^2} \right) + k_1 C_B^{n_1} - \varepsilon'' k_3 C_{G1}^{n_2} C_{C1}^{n_3} \quad (2)$$

$$\frac{\partial C_{C1}}{\partial t} = k_2 C_B^{n_1} - k_3 C_{G1}^{n_2} C_{C1}^{n_3} \quad (3)$$

$$\frac{\partial C_{G2}}{\partial t} = k_3 C_{G1}^{n_2} C_{C1}^{n_3} \quad (4)$$

$$\frac{\partial C_{C2}}{\partial t} = k_3 C_{G1}^{n_2} C_{C1}^{n_3} \quad (5)$$

Enthalpy:

$$\frac{\partial}{\partial t} (C_p \rho T) = k \left(\frac{b-1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right) - \left(D_{eG1} \frac{\partial C_{G1}}{\partial r} \right) C_{pG1} \frac{\partial T}{\partial r} + (-\Delta H) \left(-\frac{\partial \rho}{\partial t} \right) \quad (6)$$

Initial conditions:

$$t = 0; \quad C_B = C_{B0}, \quad C_{G1} = C_{C1} = C_{G2} = C_{C2} = 0, \quad T(r, 0) = T_0 \quad (7)$$

Particle boundary conditions:

$$t > 0; \quad r = 0, \quad \frac{\partial C_{G1}}{\partial r} = 0, \quad \left(\frac{\partial T}{\partial r} \right)_{r=0} = 0 \quad (8)-(9)$$

$$t > 0; \quad r = R, \quad D_{eG1} \left(\frac{\partial C_{G1}}{\partial r} \right) = k_{mG1} (C_{G10} - C_{G1}) \quad (10)$$

$$t > 0; \quad r = R, \quad k \left(\frac{\partial T}{\partial r} \right)_{r=R} = h(T_f - T) + \sigma \varepsilon (T_f^4 - T^4) \quad (11)$$

(Contd...)

Table-4. Mathematical model (Continued)

Dimensionless forms of equations (1)-(11):

$$\frac{\partial \bar{C}_B}{\partial t} = -k_1 \bar{C}_B^{n_1} - k_2 \bar{C}_B^{n_1} \quad (12)$$

$$\varepsilon'' \frac{\partial \bar{C}_{G1}}{\partial \tau} + \frac{uR}{\alpha} \frac{\partial \bar{C}_{G1}}{\partial x} = \frac{\bar{D}_{G1}}{Le} \left(\frac{b-1}{x} \frac{\partial \bar{C}_{G1}}{\partial x} + \frac{\partial^2 \bar{C}_{G1}}{\partial x^2} \right) + \frac{R^2 k_1 \bar{C}_B^{n_1}}{\alpha} - \frac{\varepsilon'' R^2 k_3 \bar{C}_{G1}^{n_2} \bar{C}_{C1}^{n_3}}{\alpha} \quad (13)$$

$$\frac{\partial \bar{C}_{C1}}{\partial t} = k_2 \bar{C}_B^{n_1} - k_3 \bar{C}_{G1}^{n_2} \bar{C}_{C1}^{n_3} \quad (14)$$

$$\frac{\partial \bar{C}_{G2}}{\partial t} = k_3 \bar{C}_{G1}^{n_2} \bar{C}_{C1}^{n_3} \quad (15)$$

$$\frac{\partial \bar{C}_{C2}}{\partial t} = k_3 \bar{C}_{G1}^{n_2} \bar{C}_{C1}^{n_3} \quad (16)$$

$$\frac{\partial \theta}{\partial \tau} = \frac{b-1}{x} \frac{\partial \theta}{\partial x} + \frac{\partial^2 \theta}{\partial x^2} + \frac{Q'' R^2 k_1}{\alpha} + \frac{1}{Le} \left(\bar{D}_{G1} \frac{\partial \bar{C}_{G1}}{\partial x} \right) \bar{C}_{pG1} \bar{C}_{B0} \frac{\partial \theta}{\partial x} \quad (17)$$

$$\tau = 0; \quad \bar{C}_B = 1, \quad \bar{C}_{G1} = \bar{C}_{C1} = \bar{C}_{G2} = \bar{C}_{C2} = 0, \quad \theta(x,0) = 1 \quad (18)$$

$$\tau > 0; \quad x = 0, \quad \frac{\partial \bar{C}_{G1}}{\partial x} = 0, \quad \frac{\partial \theta}{\partial x} = 0 \quad (19)-(20)$$

$$\tau > 0; \quad x = 1, \quad \bar{D}_{G1} \left(\frac{\partial \bar{C}_{G1}}{\partial x} \right) = Sh(\bar{C}_{G10} - \bar{C}_{G1}) \quad (21)$$

$$\tau > 0; \quad x = 1, \quad \frac{\partial \theta}{\partial x} = -\theta Bi_M \quad (22)$$

Koufopoulos *et al.* (1991) correlation:

$$h = 0.322(k/l)Pr^{1/3}Re^{0.5} \quad (23)$$

Darcy law and state equation:

$$u = -\frac{\phi}{\mu} \frac{\partial p}{\partial x} \quad (24)$$

$$p = C_{G1} R_c T / W_m \quad (25)$$

Other relations:

$$\varepsilon'' = \varepsilon_0'' + \gamma (1 - \bar{C}_B), \quad \phi = \eta \phi_B + (1 - \eta) \phi_{C1}, \quad \eta = C_B / C_{B0} \quad (26)-(28)$$

Conversion of biomass:

$$X = \frac{\bar{C}_{B0} - \left[\left(\sum_{i=1}^M \bar{C}_B \right) / (M+1) \right]}{\bar{C}_{B0}} \quad (29)$$

4.3.3 Numerical solution and Simulation

Equations (13) and (17) along with the initial and boundary conditions given by equations (18)-(22) were solved numerically by finite difference method using pure implicit scheme (Babu and Chaurasia, 2004c). The pure implicit scheme is an unconditionally stable scheme, i.e., there is no restriction on the time-step in sharp contrast with the Euler and Crank-Nicholson method as discussed by Ghoshdastidar (1998). The equations (12)-(17) are solved simultaneously. Equations (12), (14), (15), and (16) are solved by the Runge-Kutta fourth order method with both the fixed step size and the variable step size. It is found that the Runge-Kutta fourth order variable step-size method (RKVS) is faster than the Runge-Kutta fourth order method with fixed step size (RKFS), as discussed by Babu and Angira (2005). RKVS method, however, does not give the solution for a particular and fixed interval of time. The discretized form of equations (13) and (17) were solved by the Tri-Diagonal Matrix Algorithm (TDMA) also known as the Thomas Algorithm (Carnahan *et al.*, 1969).

Babu and Chaurasia (2004c) carried out simulations for the temperature ranging between 303-2100 K and the equivalent particle radius ranging between 0.0000125-0.011 m. The pyrolysis rate was obtained by considering two parallel primary reactions and a third secondary reaction between the volatile and gaseous products and char. It is found that the secondary reactions are responsible for carbon enrichment of the final residual. The effects of the parameters such as heat of reaction number, thermal conductivity, heat transfer coefficient, emissivity, and reactor temperature were analyzed. The results obtained from the model (Babu & Chaurasia, 2003a) were in good agreement with many experimental results (Shafizadeh *et al.*, 1979; Pyle & Zaror, 1984; Scott *et al.*, 1988; Alves and Figueiredo, 1989) as compared to the model developed by the earlier researchers (Bamford *et al.*, 1946; Jalan & Srivastava, 1999). It is found that the production of (char)₁ is favoured by the endothermic reactions while the production of (volatile & gases)₁ is favoured by the exothermic reactions. It is also found that the conversion time becomes successively longer as the thermal conductivity of biomass increases and/or emissivity decreases, thus affecting the reactor throughput. It is observed that the feedstocks with lower thermal conductivity produces a gas of better quality for a fixed particle size. Babu and Chaurasia (2004c) also performed sensitivity analysis for most of the variables and it is found that convective heat transfer coefficient is the least sensitive parameter and sensitivity for all the parameters is highest for the slab geometry and is lowest for the spherical geometry. The results obtained by Babu and Chaurasia (2004c) have a lot of practical importance and physical significance in industrial pyrolysis applications. The results are also important and useful for design of biomass gasifiers, reactors, etc.

5. Thermal Plasma Pyrolysis

Thermal plasma pyrolysis can be described as the process of reacting a carbonaceous solid with limited amounts of oxygen at very high temperature to produce gas and solid products. In the highly reactive plasma zone, there is a large fraction of electrons, ions and excited molecules together with the high-energy radiation. When carbonaceous particles are injected into plasma, they are heated very rapidly by the plasma; and the volatile matter is released and cracked giving rise to hydrogen and light hydrocarbons

such as methane and acetylene. There are four stages can be distinguished in the thermal plasma pyrolysis process:

Stage – 1. A very fast heating of the particles as a result of their heat exchange with the plasma jet.

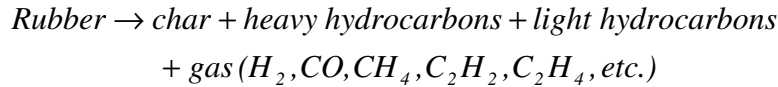
Stage – 2. An explosive liberation of volatile matter from the particles.

Stage – 3. A very quick gasification of the homogeneous phase and rapid heat and mass exchange.

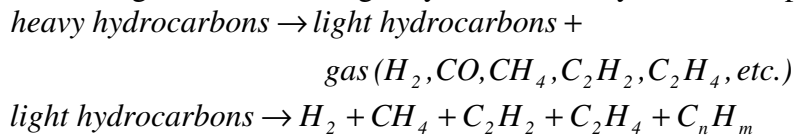
Stage – 4. Further gasification of char particles with various gaseous components.

A reaction scheme proposed by Huang *et al.* (2003) for rubber pyrolysis in a dc arc plasma can be divided in four stages as described below:

In *Stage – 1*, primary pyrolysis reactions take place and the volatile matter is released including heavy hydrocarbons (tar), light hydrocarbons, and other gaseous components, leaving behind solid char.

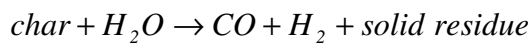


In *Stage – 2*, Tar get cracked and light hydrocarbon may also decompose



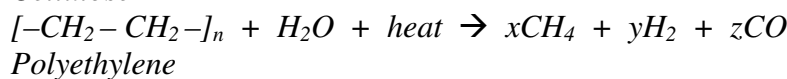
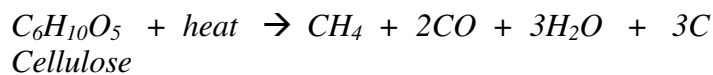
In *Stage – 3*, light hydrocarbons may further decompose. This Stage could be replaced by quench technology in order to achieve certain technical purposes such as monomer recovery.

In *Stage – 4*, addition of water/steam could be effectively used to promote syngas (H₂ and CO) production.



This could be one of the reasons for the observation that H₂ and CO concentrations were increased, and solid yield decreased with steam injection. The solid residue includes the inorganic tire component, carbon black filler, and carbonaceous deposit (Huang *et al.*, 2003).

Nema and Prasad (2002) proposed following reactions for the plasma pyrolysis of simulated medical waste.



High temperature combined with the high heating rate of the plasma results in the destruction of organic waste, giving rise to a gas and a solid residue with varied

properties depending on the feed characteristics and operating conditions (Huang and Tang, 2007).

5.1 Reaction Mechanisms of plasma assisted Pyrolysis

The pyrolysis mechanisms of polymer molecules, which may comprise tens of thousands of atoms, are very complex. Pyrolytic reactions have been broadly classified into four groups: random main-chain scission, depolymerization, carbonization, and side-group reactions. Random-chain scission is defined as breaking of the main chain to produce smaller molecules of random sizes. Depolymerization is defined as the successive removal of monomer units from the chain and leads to the formation of free radicals and chain reactions. Carbonization and side-group reactions include those reactions, which lead to cross-linking, straight chain polymer formation by elimination of side chains, cyclization, and aromatization by dehydrogenation. According to free-radical chain-reaction theory both chain scission and depolymerization mechanisms involve initiation, propagation, chain transfer, and termination reactions.

Based on the standard Gibbs free energy changes for the reactions, it is found that energy requirement for carbon-carbon bond cleavage is less than those for hydrogen abstraction. At a given temperature, chain scission of C-C bonds at the ends of molecules is more probable than at the center of the molecule. Based on the bond dissociation energies of C-C and C-H bonds, it is found that the C-C and C-H bonds to the allylic carbon are weaker than the corresponding bonds in a pure saturated chain. These bonds are β -bonds with respect to the double bond and their scission is known as β -scission. All chain ends of heavy molecular weight polyethylene have β -bond. Collisions between the polymer molecules and electrons and ions from the plasma initiate the β -scission process in plasma reactor. Propagation occurs through a series of reactions which convert the polymer fragments into reactants and, subsequently, to final products through radical decomposition, radical isomerization, hydrogen transfer, and/or radical addition. Termination reactions occur when two radicals combine or disproportionate to form stable products (Guddeti *et al.*, 2000).

The range of product compositions obtained will depend on both the relative sensitivity of secondary versus primary reactions to changes in temperature and the residence time of the material within the high-temperature plasma region.

5.2 Kinetic Modeling of Plasma Pyrolysis

Experimental studies on plasma pyrolysis have been conducted by many researchers using variety of raw materials such as agricultural residue, waste tyre, municipal solid waste etc. (Guddeti *et al.*, 2000; Huang *et al.*, 2003; Shuangning *et al.*, 2006; Huang and Tang, 2007; Hung-Lung *et al.*, 2007). Understanding the physical phenomena of plasma assisted pyrolysis and representing them with an appropriate mathematical model is essential in the design of reactors.

Shuangning *et al.* (2006) developed a plasma heated laminar entrained flow reactor (PHLEFR) in order to study the volatilization characteristics of biomass particles at flash heating rates. A simple kinetic model is proposed in order to predict the reaction rate for

wide range of operating condition and various biomasses. The conversion process is mathematically expressed by a following equation.

$$\frac{d\alpha}{dt} = A e^{-\frac{E}{RT}} (1 - \alpha)$$

where α is the fraction of reactant decomposed at residence time t . A and E are the apparent frequency factor (s^{-1}) and apparent activation energy (kJ/mol), respectively; R is the universal gas constant, 8.3145 (J/mol); T is the absolute temperature (K) of the pyrolytic process. The fractional reactant α is defined as the ratio of W to W^{∞} , where W is the volatile mass fraction at time t ; W^{∞} is the maximum volatile mass fraction (in wt%). The kinetic model presented here was fitted to the experimental data and kinetic parameters are found (Table – 5).

Table-5. Kinetic Parameters of biomass pyrolysis reaction determined with PHLEFR

Raw Materials	A (s^{-1}) (10^3)	E (kJ/mol)
Wheat Straw	1.05	31.63
Coconut Shell	6.84	48.73
Rice Husk	1.19	39.30
Cotton stalk	2.44	40.84

Shuangning *et al.* (2006) studied the volatilization characteristics of biomass particles at flash heating rates and developed and validated the kinetic model and found the kinetic parameters for the various agricultural residues. However this analysis is not reported in the literature for other carbonaceous wastes and as well the model developed by Shuangning *et al.* (2006) is not improved to incorporate the effects of various parameters such as feed rate, size of the particles, heating rate, thermal and thermodynamic properties (thermal conductivity, heat transfer coefficient, emissivity and heat of reaction number) of the feedstock on the convective-radiant pyrolysis of biomass fuels.

6. Concluding Remarks

Thermal plasma pyrolysis is in the forefront of modern waste treatment. There is great potential for development of thermal plasma pyrolysis technologies applicable to waste management with energy and material recovery. Although important experimental studies have been carried out in recent years, there are still considerable technical challenges to be faced in developing and modifying thermal plasma pyrolysis processes for industrial applications. Apart from the experimental investigation, kinetic modeling and simulation is required to describe the plasma pyrolysis mathematically. It would be useful to predict the product gas concentration for various operating conditions and for a variety of feed mixtures. There is a great scope of study in modeling and simulation of plasma pyrolysis to design a suitable plasma pyrolysis reactor.

Nomenclature

A_1, A_2, A_3	frequency factor, s^{-1}
b	geometry factor (slab=1, cylinder=2, sphere=3)
B	virgin biomass
G_1	(gases and volatiles) ₁
C_1	(char) ₁
G_2	(gases and volatiles) ₂
C_2	(char) ₂
C_B	concentration of B , C_{B0} at initial condition, $kg\ m^{-3}$
C_{G1}	concentration of G_1 , C_{G10} at initial condition, $kg\ m^{-3}$
C_{C1}	concentration of C_1 , C_{C10} at initial condition, $kg\ m^{-3}$
C_{G2}	concentration of G_2 , C_{G20} at initial condition, $kg\ m^{-3}$
C_{C2}	concentration of C_2 , C_{C20} at initial condition, $kg\ m^{-3}$
C_p	specific heat capacity, $J\ kg^{-1}\ K^{-1}$
C_{pG1}	heat capacity of (gases and volatiles) ₁ , C_{pG10} at initial condition, $J\ mol^{-1}\ K^{-1}$
D_1, D_2	constants defined by expressions of k_1 and k_2 respectively, K
D_{eG1}	effective diffusivity of (gases and volatiles) ₁ , D_{eG10} for initial effective diffusivity, $m^2\ s^{-1}$
E_3	activation energy defined by expression of k_3 , $J\ mol^{-1}$
h	convective heat transfer coefficient, $W\ m^{-2}\ K^{-1}$
k	thermal conductivity, $W\ m^{-1}\ K^{-1}$
k_{mG1}	mass transfer coefficient of (gases and volatiles) ₁ across the film, $m\ s^{-1}$
k_1, k_2, k_3	rate constants, s^{-1}
l	axial length of cylinder, m
L_1, L_2	constants defined by expressions of k_1 and k_2 respectively, K^2
M	total number of equations used in the simulation of the model
n_1, n_2, n_3	orders of reactions
p	gas pressure, Nm^{-2}
P_1, P_2	variation constants of the parameters defined
Q	heat of reaction number, $m^3\ kg^{-1}$
r	radial distance, m
R	radius for cylinder and sphere; half thickness for slab, m
R_c	universal gas constant, $J\ mol^{-1}$
t	time, s
T	temperature, K
u	gas velocity, $m\ s^{-1}$
W_i	molecular weight of species i , $kg\ mol^{-1}$
x	dimensionless radial distance
X	conversion of biomass

Nomenclature (Continued)

Greek letters

ΔH	heat of reaction, J kg ⁻¹
$\Delta \tau$	axial grid length
Δx	radial grid distance
ρ	density, ρ_0 at initial condition, kg m ⁻³
α	thermal diffusivity, m ² s ⁻¹
τ	dimensionless time
γ	constant defined by equation (26)
θ	normalized temperature
ε	emissivity coefficient
ε''	void fraction of particle as defined by equation (26), ε_0'' at initial condition
σ	Stefan Boltzmann constant, W m ⁻² K ⁻⁴
ϕ	permeability, m ²
η	reaction progress variable
μ	viscosity, kg m ⁻¹ s ⁻¹

Dimensionless numbers

Bi_M	Modified Biot number
Le	Lewis number
Pr	Prandtl number
Q''	Heat of reaction number
Re	Reynolds number
Sh	Sherwood number

Subscripts

g	gas
0	initial
f	final
V	water vapor
L	light hydrocarbons
B	wood
m	mean

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